EFFECT OF FIBRE TEXTILE REINFORCEMENT ON ANIONIC POLYAMIDE-6 COMPOSITE PROPERTIES

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Abstract

To explore the potential of fibre-reinforced thermoplastic anionic polyamide-6 composites for lightweight structures, the effect of the fibre addition needed to be investigated. The reactive processing of neat anionic polyamide-6 (APA-6) has been investigated and it was demonstrated that it exhibited excellent resin properties.

The addition of 70% wt of preheated E-glass fibres altered the heat transfer to the resin. Consequently, the overall internally produced heat decreased and needed to be compensated for by a higher external heat to get the same properties as the neat resin. Due to the high thermal conductivity of the preheated fibres also a reduction of the infusion window was observed. Besides the change in properties of the laminates, a temperature gradient in flow direction resulting in different resin properties from inlet to outlet of the composite.

1 Introduction

Nowadays, the development and use of textile fibre reinforced thermoplastic composites for lightweight structures has become more and more important. Thermoplastic composites have several advantages compared to their thermoset counterparts: lower processing times, the easy assembly of parts through welding, recyclability and high toughness.

In order to produce thicker and bigger thermoplastic parts, the traditional melt processing technique is substituted by a vacuum infusion process. To overcome the high resin viscosity, a reactive resin system, which has been developed at the TUDelft, was used for the vacuum infusion of the anionic polyamide-6 thermoplastic composites. The high molecular weight APA-6 is obtained through ring-opening polymerisation. The reactive processing used, combines all the manufacturing steps into one single production step: after vacuum infusion of the reactive mixture into the fibre preform, a delayed in-situ polymerisation of the monomer takes place to the high molecular weight thermoplastic polymer. When demoulding the composite, one hour after infusion, the cured, fully recyclable thermoplastic composite part is obtained.

It was shown in previous studies that the anionic polyamide-6 (APA-6) resin exhibited excellent mechanical properties and demonstrated its potential as a composite matrix [7]. Within this research, the addition of textile fibre mats to this resin system was investigated as well as its effect on the heat transfer and the composite properties.

2 Materials and processing methods

2.1 Materials

2.1.1 Resin material

For the vacuum infusion of the anionic polyamide-6 thermoplastic laminates, a reactive resin mixture is used, which consists of three components: monomer, activator and initiator. The anionic polymerisation grade ε-caprolactam monomer (APCaprolactam) was supplied by Brüggemann Chemicals, Germany. As the monomer is extremely sensitive to moisture, it was stored at 50°C under atmospheric conditions to prevent sublimation and recrystallisation of the monomer flakes as well as exposure to moisture.

The combination of the activator and the initiator and their relative dose with respect to the monomer content was chosen by van Rijswijk et al. [6]. The reaction of the activator/initiator combination used is slow initially, leading to a low viscous resin mixture at the beginning of the reaction, hereby guaranteeing sufficient time for

the full wet-out of the fibre preform. The resin mixture for this study consists of 1,2% mol of the difunctional hexamethylene-1,6-dicarbamoylcaprolactam activator and 1,2%mol of the initiator caprolactam magnesium bromide, NYRIM® C1. Both the activator and the initiator were supplied by Brüggemann Chemicals, Germany and are stored under a nitrogen atmosphere in sealed polyethylene lined aluminium drums. The chemical structure of the different components for the APA-6 resin can be seen in Fig. 1. The polymerisation process to the anionic polyamide-6 is given in Fig. 2.

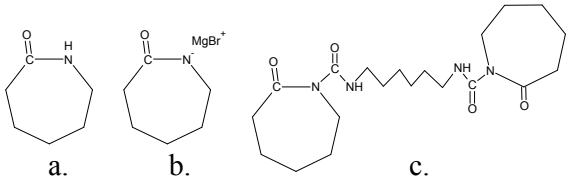

Fig. 1. Chemical structure of (a.) caprolactam, (b.) caprolactam magnesium bromide and (c.) hexamethylene-1,6-dicarbamoylcaprolactam

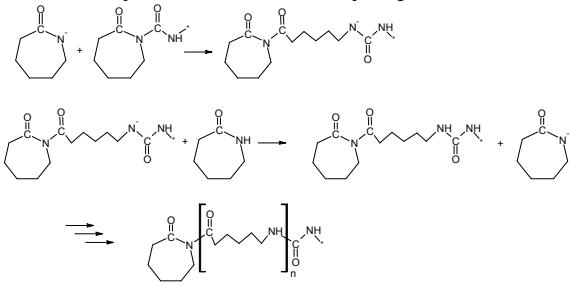

Fig. 2. Anionic polymerisation process of caprolactam into polyamide-6

2.1.2 Glass fibres

E-glass fibre mats are used to reinforce the APA-6 composites. The 8-harness satin weave E-glass fabrics (SS 0303 050, weave style 7781, 300 gram/m^2) were supplied by Ten Cate Advanced Composites bv., Nijverdal, The Netherlands. The chemical structure of the aminosilane sized glass fibres is presented in Fig. 3.

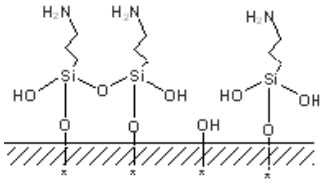

Fig. 3. Aminosilane sized E-glass fibres

2.2 Processing

2.2.1 Mixing different components resin

A special designed lab-scale mixing unit (Mini Mixing Unit 'MMU-TUDelft', Bronk Industrial b.v., The Netherlands) is used to prepare the resin mixture for infusion. This MMU consists of two separate tanks: one for the monomer/activator mixture and the other for the monomer/initiator mixture, both under a nitrogen atmosphere and at a temperature of 110°C. Both mixtures are melted, mixed and recirculated separately in the MMU during preparation. Then, the volume needed for the infusion of a laminate is dispensed in a 1:1 ratio and mixed by a static mixer into the buffer vessel (resin reservoir). This buffer vessel is put in a special designed aluminium cylinder, which is placed on a heated plate to keep the vessel and resin mixture at a temperature of 110°C during infusion.

2.2.2 Infusion

A balanced, symmetric 12-ply laminate is prepared for vacuum infusion and is placed between a hot platen press, which is the heating device for the production of the neat resin panels and the laminates. The dry fibre perform is then heated to the required processing temperature (between 150°C-190°C). Before infusion of the laminate can take place, the resin mixture in the buffer vessel is degassed to remove N_2 dissolved in the mixture during storage in the MMU tanks. After degassing, the resin is allowed to flow through the inlet line-injection into the laminate. The resin injection and fibre compaction are achieved under vacuum. When the resin reaches the line-injection outlet, the resin inlet tube is closed and the part is ready to cure. The vacuum is maintained during the cure cycle of one hour.

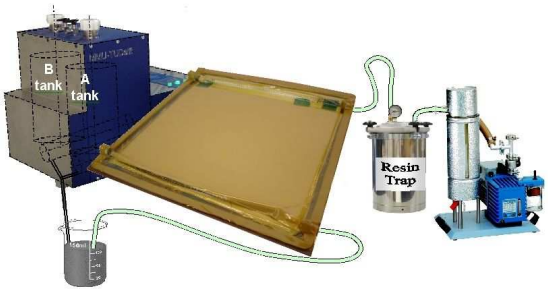

Fig. 4. Vacuum infusion set-up (from left to right: Mini Mixing Unit, buffer vessel, laminate and heating device, resin trap and vacuum pump

3 Analysis methods

The analysis methods for both neat panels and laminates are described in this section.

3.1 Degree of conversion

To determine the degree of conversion (DOC) of the polymer, samples of the composite plate are taken at 5 cm from the resin inlet and outlet, by means of a drill. After drying the samples at 50°C in a vacuum oven, they are weighed (m_{tot}). Next, the samples are refluxed overnight in demineralised water. During this process, the monomer dissolves and after drying of the residue, the mass of the polymer and fibres ($m_{pol+fib}$) is measured and the mass of the monomer (m_{mon}) can be calculated. To be able to calculate the degree of conversion of the polymer, one needs to know the mass of the fibres of the sample. Therefore, the samples were burned off in a carbolite oven at 565°C for one hour; according to ASTM D 2584–02 [1] and the fibre weight (m_{fib}) can be obtained. The actual degree of conversion can be calculated as follows:

$$DOC = \left(1 - \frac{m_{mon}}{m_{tot} - m_{fib}}\right) \times 100\% \qquad (3.1)$$

It should be taken into account that low molecular oligomers formed during polymerisation will also dissolve during the reflux process [8]. These oligomers as well as the unreacted monomer do not have load carrying capabilities either. Equation 4.1 will thus not give the exact degree of conversion, but will give a good idea of the amount of non-load carrying substances in the composite.

3.2 Degree of crystallinity

The degree of crystallinity (X_c) and the melting temperature (T_m) of the polymer are determined by means of a Perkin Elmer Differential Scanning Calorimeter (DSC). Disc-shaped samples (m_{sp}) of approximately 5 mg are taken from the laminate at the same location as the degree of conversion samples and are dried overnight. In the DSC, the test sample is held at 25°C for two minutes and is then heated up to 240°C at a rate of 10°C per minute. The results had to be corrected for the fibre content of the sample. Therefore, the fibre content (m_{fib}) was determined by burning off the resin after the DSC test [1]. The degree of crystallinity can now be calculated as follows:

$$X_c = \frac{\Delta H_m}{\Delta H_{100}} \cdot \frac{1}{m_{sp} - m_{fib}} \cdot \frac{1}{DOC} \times 100\% \qquad (3.2)$$

In which: ΔH_m is the melting enthalpy of the specimen [J/g]; ΔH_{100} is the melting enthalpy of a fully crystalline polyamide-6 = 190 J/g [2]. The third term in equation 4.2 is a correction factor for the degree of conversion of the sample.

3.3 Ultrasonic analysis

To check the homogeneity of the laminate, a high frequency (10 MHz) ultrasonic C-scan was used. A single through transmission mode was used to analyse the differences within the material, with water as a contact medium. Scans were performed at a speed of 352 mm/s to obtain images with a grid length of 0.5 mm and a width of 1 mm and were analyzed using ALIS software.

3.4 Temperature measurements

Both the polymerisation and crystallisation process involve an exothermal reaction [3]. To observe the temperature behaviour of the laminate during infusion and cure, a temperature logging test has been done. Thermocouples were positioned at several locations in the laminate, between glass fabric layer 6 and 7.

4 Effect of fibre addition on heat transfer

Previous research by van Rijswijk et al. [5, 7] showed that polymerisation temperature is one of the most important processing parameters for the APA-6 resin system. The investigation concerning the change in heat transfer due to the addition of the fibre textiles is thus of great importance. The thermal properties of the APA-6 resin, the E-glass fibre textiles and the composite (based on a fibre volume fraction of 50%) are listed in Table 1 and Table 2.

Table 1. Thermal properties (Source: DSM Fibre Intermediates, The Netherlands and Rigo et al. [4])

Material	Density[1] *[kg/m³]*	Conductivity[1] *[J/(s·m·°C)]*	Specific heat[1] *[J/(kg·°C)]*
Caprolactam[1]	950	0.14	2500
Anionic polyamide-6[1]	1130	0.2	2250
Glass fibre	2525	1	840
Composite[2, 3]	1760-1912	0.57-0.6	1670-1545

Table 2. Thermal properties ctd. (Source: DSM Fibre Intermediates, The Netherlands and Rigo et al. [4])

Material	ΔH_{pol} *[J/g]*	ΔH_{cryst} *[J/g]*
Caprolactam[1]	-	-
Anionic polyamide-6[1]	166	144
Glass fibre	-	-
Composite[2, 3]	47	41

[1] Measured at 150ºC
[2] Based on a final conversion of 100% and a final crystallinity of 40%
[3] Based on a glass fibre volume content of 50%, values given for both unreacted and fully reacted matrix

4.1 Thermal conductivity

As can be derived from Table 1, the pre-heated fibres exhibit a high thermal conductivity. By applying the rule of mixtures, it can be seen that the overall conductivity of the composite is higher than for the neat resin, therefore leading to a faster warming of the reinforced resin system. Previous research showed that at higher processing temperatures, the polymerisation reaction is accelerated [5]. The exothermic peak temperatures of the APA-6 neat resin were found at 10-20 min (depending on the processing temperature) [7] whereas for the APA-6 composites, these peaks were found 5-8 min earlier, as can be seen in Fig. 5. The presence of the pre-heated fibres and the higher conductivity of the impregnated fibres therefore results in a significant reduction of the infusion window.

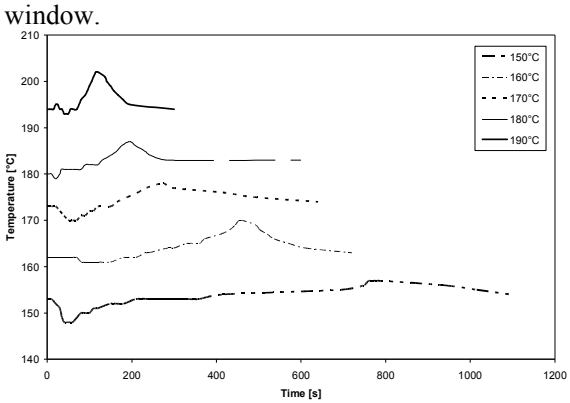

Fig. 5. Temperature logging of the infusion (t=0sec) and reaction of APA-6 composites at different processing temperature (150-190°C) measured in the middle of the composite.

4.2 Exothermal peaks

Since both polymerisation and crystallisation are exothermic, a temperature rise can be observed when reaction takes place. From the thermocouple measurements in Fig. 5, the temperature increase due to the reaction exotherms could be obtained. This increase in temperature was in the range of 5-10°C for the composites, whereas for the neat resin samples the temperature rise was in the order of 10-30°C (depending on the reaction rate and the thickness of the sample). The difference between the neat resin samples and the composites can be explained by the fact that the resin in the composites only occupies 30% of the total weight and therefore the internally produced heat per unit weight during polymerisation (ΔH_{pol}) and crystallisation (ΔH_{cryst}) is reduced to less than a third, see Table 2. This lower internally produced heat has several consequences on the heat transfer of the system and consequently on the properties of the composites, as will be discussed in the next paragraph.

5 Effect on properties

The lower internally produced heat of the resin system of the fibre reinforced APA-6 composites results in differences in properties between the neat resin and the composite. Due to the lower reaction rate of the resin of the reinforced composite, a lower degree of conversion is obtained at all processing temperatures, see Fig. 6.

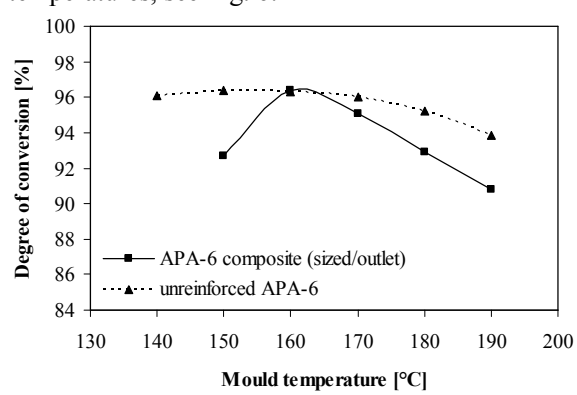

Fig. 6. Degree of conversion unreinforced APA-6 and reinforced APA-6 composites

Due to the lower overall heat of the resin system when glass fibre reinforced, the tendency for the polymer to crystallize would be higher. The growth of the crystal from a nucleus is strongly dependent on the processing temperature. At low processing temperatures, the difference in free

enthalpy between the liquid and crystal is high, which is the thermodynamic driving force to crystallise [9]. As a consequence, the rate of crystal growth increases and results in a higher degree of crystallinity. As can be observed in Fig. 7, this is true at low processing temperatures (150 - 170°C). At the same mould temperature a higher degree of crystallinity is measured for the composite. However, at higher processing temperatures, the fibre-to-matrix bond improves, hindering the crystal growth and therefore resulting in a lower degree of crystallinity.

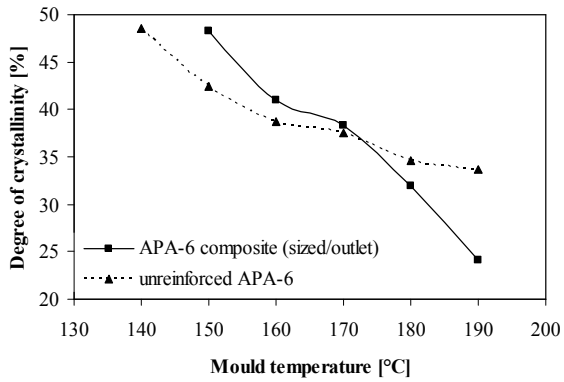

Fig. 7. Degree of crystallinity unreinforced APA-6 and reinforced APA-6 composites

The optimal combination of degree of conversion and crystallinity of the neat resin was found at a processing temperature of 150°C [5], whereas the optimum in resin properties for the composite are found at a processing temperature of 160°C, as can be seen in Fig. 6 and Fig. 7. A higher external heat is thus necessary to compensate for the lower internally produced heat.

6 Gradient in flow direction

During impregnation of the laminate, the resin from the buffer vessel is at a temperature of 110°C, whereas the fibre bed itself is at the required processing temperature, 150-190°C. When infused, the resin at the outlet will be at a higher temperature than at the inlet, as it passed through the fibre bed at the processing temperature. Due to this temperature gradient, differences in properties between the inlet and the outlet of the laminate arise.

The lower temperature at the inlet of the laminate is translated in a higher crystallinity, as can be observed in Fig. 8. Due to the fact that the resin at the inlet is colder than at the outlet, the thermodynamic driving force to crystallize will be higher. Therefore, the rate of crystal growth at the inlet increases, as discussed in the previous section.

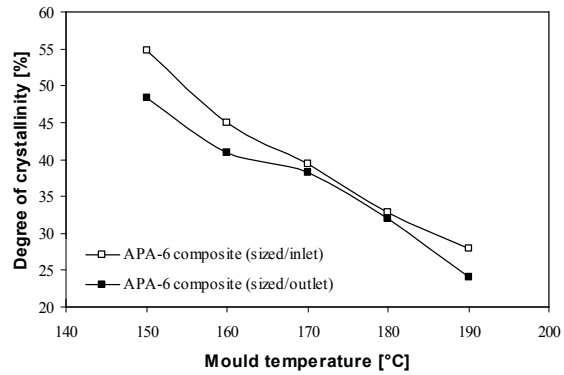

Fig. 8. Degree of crystallinity of the inlet and the outlet of a vacuum-infused APA-6 composite

Because of the higher temperatures at the resin outlet, the polymerisation as well as the crystallisation process will start at the outlet of the laminate. The reaction will then move in the direction of the inlet in opposite flow direction, as can be seen in Fig. 9, in which the peaks represent the polymerisation exothermal reaction.

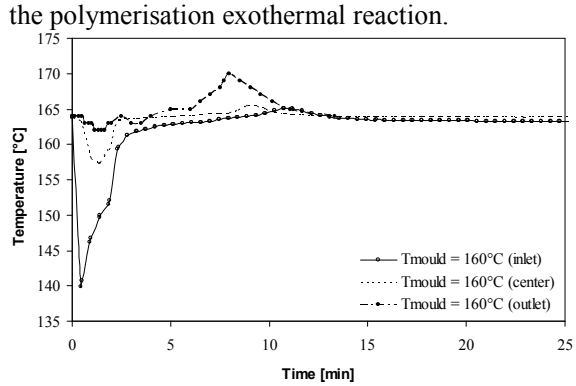

Fig. 9. Temperature logging of the infusion (t=0sec) and reaction of a laminate at 160C at three locations: resin inlet, middle and resin outlet.

Another issue regarding the quality of the laminate is the entrapment of air. In-mould degassing of residual air or nitrogen bubbles in the laminate is hindered by:

- The fast impregnation of the laminate due to the water-like viscosity of the resin (a 12-ply, 25x25 cm^2 laminate is infused within two minutes)
- The dense fibre textile structure
- The fact that the polymerisation starts at the resin outlet and moves in the opposite flow direction, causing the air to be trapped near the resin inlet.

To investigate this entrapment of air, C-scan images were generated to inspect the quality of the laminate. A typical C-scan image of a vacuum infused APA-6 composite is shown in Fig. 10 and shows that the inlet of the laminate is a void-rich area, whereas the outlet consolidated well.

The temperature gradient due to infusion of a relatively cold resin in a heated fibre bed not only causes differences in resin properties between the inlet and outlet of the laminate but also induces a quality difference due to entrapment of voids near the inlet of the laminate. This entrapment is mainly caused by the polymerisation process starting at the resin outlet and moving in opposite flow direction.

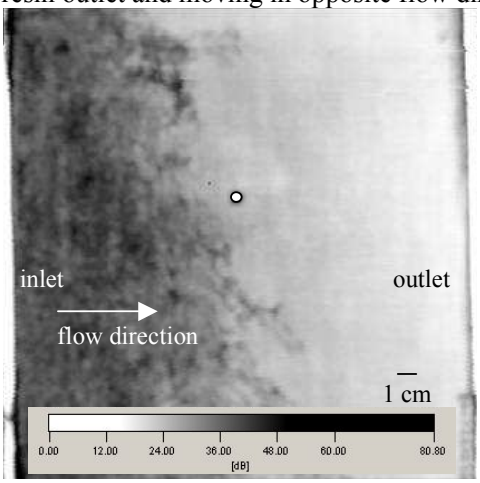

Fig. 10. Typical C-scan image of a vacuum infused APA-6 composite: Dark areas represent void-rich areas, whereas the white dot in the centre is a reference point used during the scanning procedure.

7 Conclusions and recommendations

7.1 Conclusions

Within this research, the addition of textile fibre mats to the APA-6 resin system was investigated. It was shown that differences occurred in the heat transfer when comparing the neat resin and the composite samples. This led to the following conclusions for the resin in the composites:

- Less overall heat to the system.

A shift of resin properties was observed with respect to temperature, when comparing the neat resin and composite properties. At the same mould temperature, higher degree of crystallinity was obtained in the composites. The decrease in internally produced heat in the system thus has to be compensated for by a higher external heat. Whereas the optimal temperature for the neat resin samples was found at 150°C, for the composites the optimal processing temperature is at 160°C.

- Lower reaction rate.

A lower reaction rate results in a lower degree of conversion for the composites when compared to the neat resin at the same mould temperature.

- Reduced infusion window.

Due to the addition of pre-heated fibres to the resin, which exhibit a high thermal conductivity, leading to a faster warming of the reinforced resin system and therefore to a significant reduction of the infusion window.

The addition of fibre textile to the resin system not only influences the properties of the composite but also induces a gradient in flow direction of the laminate. Due to the infusion of the relatively cold resin into the hot mould with pre-heated fibres and the restriction of convection flows by the dense fiber fabrics, a temperature gradient from cold to hot is established just after infusion.

7.2 Recommendations

In order to produce homogeneous laminates, less difference in temperature between the pre-heated fibres and the resin needs to be established. It is therefore of importance to investigate different heating techniques. The control of the resin flow velocity is also of importance for in-mould degassing and needs attention in following research.

Acknowledgements

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References

[1] ASTM D2584-02: Standard Test Method for Ignition Loss of Cured Reinforced Resins.

[2] H. Cartledge and C.A. Baillie. “Study of microstructural and mechnical properties of nylon/glass composite. Part i. The effect of thermal processing on crystallinity, transcrystallinity and crystal phases”. *Journal of Materials Science*, Vol. 34, No. 20, pp 5099-5111, 1999.

[3] A.A. van Geenen. Anionic polyamide 6 - chemistry and processing. Internal report, DSM Plastics, 2002.

[4] Rigo A, Fabbri G, Talamini G. "Kinetic Study of Anionic Polymerization of 6-Caprolactam by Differential Calorimetry". *Polymer Letters Edition,* Vol. 13, pp 469-477, 1975.

[5] Van Rijswijk K, Bersee HEN, Beukers A, Picken SJ, Van Geenen AA. "Optimisation of Anionic Polyamide-6 for Vacuum Infusion of Thermoplastic Composites: Influence of Polymerisation Temperature on Matrix Properties". *Polymer Testing,* Vol. 25, No. 3, pp 392-404, 2005.

[6] Van Rijswijk K, Bersee HEN, Jager WF, Picken SJ. "Optimisation of Anionic Polyamide-6 for Vacuum Infusion of Thermoplastic Composites: Choice of Activator and Initiator". *Composites Part A: Applied Science and Manufacturing,* Vol. 37, pp 949-956, 2005.

[7] Van Rijswijk K, Lindstedt S, Vlasveld DPN, Bersee HEN, Beukers A. "Reactive processing of anionic polyamide-6 for application in fiber composites: a comparative study with melt processed polyamides and nanocomposites". *Polymer Testing,* Vol. 25, No. 7, pp 873-887, 2006.

[8] K. Ueda, M. Hosoda, T. Madsuda, and K. Tai. "Synthesis of high molecular weight nylon 6 by anionic polymerization of ε-caprolactam. Formation of cyclic oligomers". *Polymer Journal*, Vol. 30, No. 3, pp 186-191, 1998.

[9] A.K. van der Vegt. "*From Polymers to Plastics"*. DUP Blue Print, 2002.